

THIN-LAYER-COVERED MULTILAYER GOLF BALL

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of co-pending Application No. 09/274,015, filed March 22, 1999, which is a continuation-in-part of U.S. Patent No. 5,885,172, and a continuation-in-part of co-pending Application No. 09/721,740, filed November 27, 2000, which is a continuation-in-part of co-pending Application No. 09/311,591, filed May 14, 1999, and Application No. 09/461,736, filed December 16, 1999, each of which is incorporated herein in its entirety by reference.

FIELD OF THE INVENTION

This invention relates generally to golf balls, and more specifically, to multilayer golf balls. In particular, this invention relates to a golf ball having a core comprising a center and an outer core layer, and a cover comprising an inner cover layer and a thin outer cover layer. The outer cover layer is formed of a thermoset material formed from a castable, reactive liquid. The core is formed of a polybutadiene composition comprising a butadiene polymer with a resilience index greater than about 40 and a molecular weight greater than about 200,000.

BACKGROUND OF THE INVENTION

Conventional golf balls can be divided into several general classes: (a) solid golf balls having one or more layers, and (b) wound golf balls. Solid golf balls include one-piece balls, which are easy to construct and relatively inexpensive, but have poor playing characteristics and are thus generally limited for use as range balls. Two-piece balls are constructed with a generally solid core and a cover and are generally the most popular with recreational golfers because they are very durable and provide maximum distance. Typically, the core is formed from polybutadiene that is chemically crosslinked with zinc diacrylate and/or other similar crosslinking agents. These balls are generally easy to manufacture, but are regarded as having limited playing characteristics. Solid golf balls also include multi-layer golf balls that are comprised of a solid core of one or more layers and/or a cover of one or more layers. These balls are regarded as having an extended range of playing characteristics.

Wound golf balls are generally preferred by many players due to their high spin and soft “feel” characteristics. Wound golf balls typically include a solid, hollow, or fluid-filled center, surrounded by a tensioned elastomeric material, and a cover. Wound balls generally are more difficult and expensive to manufacture than solid two-piece balls.

A variety of golf balls have been designed by manufacturers to provide a wide range of playing characteristics, such as compression, velocity, “feel,” and spin. These characteristics can be optimized for various playing abilities. For example, one component that manufacturers commonly alter to change the playing characteristics of golf balls is the polymer composition used to form golf ball centers and/or cores. One of the most common polymers employed is polybutadiene and, more specifically, polybutadiene having a high cis- isomer concentration.

The use of a polybutadiene having a high cis- concentration results in a very resilient and rigid golf ball, especially when coupled with a hard cover material. These highly resilient golf balls have a relatively hard “feel” when struck by a club. Soft “feel” golf balls constructed with a high cis-polybutadiene have low resilience. In an effort to provide improved golf balls, various other polybutadiene formulations have been prepared, as discussed below.

U.S. Patent No. 3,239,228 discloses a solid golf ball having a core molded of polybutadiene rubber with a high sulfur content, and a cover. The polybutadiene content of the core is stereo-controlled to the configuration 25-100 percent cis- and 0-65 percent trans- 1,4-polybutadiene, with any remainder having a vinyl configuration of polybutadiene. A preferred embodiment of the polybutadiene golf ball core contains 35 percent cis-, 52 percent trans-, and 13 percent vinyl-polybutadiene. The level of trans- and vinyl- content are disclosed to be unimportant to the overall playing characteristics of the polymer blend.

British Patent No. 1,168,609 discloses a molding composition from which improved golf ball cores can be molded and which contains cis-polybutadiene as a basic polymer component. The core polymer component typically includes at least 60 percent cis-polybutadiene, with the remainder being either the trans- or vinyl- forms of polybutadiene. In a preferred embodiment, the core polybutadiene component contains 90 percent cis- configuration, with the remaining 10 percent being either the trans- or vinyl- configurations of 1,4-polybutadiene.

U.S. Patent Nos. 3,572,721 and 3,572,722 disclose a solid, one- or two-piece golf ball, with the two-piece ball having a core and a cover. The cover material can include any one of a number of materials, or blends thereof, known to those of ordinary skill in the art, including

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U.S. Patent No. 3,992,014 discloses a one-piece, solid golf ball. The golf ball material is typically polybutadiene, with a stereo-configuration selected to be at least 60 percent cis-polybutadiene, with the remaining 40 percent being the trans-polybutadiene and/or 1,2-polybutadiene (vinyl) isomers.

U.S. Patent No. 4,931,376 discloses a process for producing butadiene polymers for use in various applications, including golf ball cover materials. One embodiment of the invention employs a blended polymeric resin material, including at least 30 percent by weight of a trans-polybutadiene polymer as a golf ball cover on a two-piece ball. In a preferred embodiment, the golf ball cover material contains a blend including 30 to 90 percent by weight of a trans-polybutadiene polymer.

U.S. Patent No. 4,971,329 discloses a solid golf ball made from a polybutadiene admixture of cis-1,4 polybutadiene and 1,2 polybutadiene, a metal salt of an unsaturated carboxylic acid, an inorganic filler, and a free radical initiator. The admixture has about 99.5 percent to about 95 percent by weight of cis-1,4 polybutadiene and about 0.5 percent to about 5 percent by weight of 1,2 polybutadiene.

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from about 0.05 to 2 parts per hundred by weight and the organic peroxide is typically present in an amount from about 0.5 to 3 parts per hundred by weight of the total polymer component.

European Patent No. 0 577 058 discloses a golf ball containing a core and a cover that is formed as two separate layers. The inner layer of the cover is molded over the core and is formed from ionomer resin. The outer layer of the cover is molded over the inner layer and is formed from a blend of natural or synthetic balata and a crosslinkable elastomer, such as polybutadiene. In one embodiment of the outer layer of the cover, the elastomer is 1,4-polybutadiene having a cis- structure of at least 40 percent, with the remaining 60 percent being the trans- isomer. A preferred embodiment contains a cis- structure of at least 90 percent and more preferably, a cis- structure of at least 95 percent.

U.S. Patent No. 5,421,580 discloses a wound golf ball having a liquid center contained in a center bag, a rubber thread layer formed on the liquid center, and a cover over the wound layer and liquid center. The cover material can include any one of a number of materials, or blends thereof, known to those of ordinary skill in the art, including trans-polybutadiene and/or 1,2-polybutadiene (vinyl), such that the cover has a JIS-C hardness of 70-85; preferred trans-percentages are not disclosed.

U.S. Patent No. 5,697,856 discloses a solid golf ball having a core and a cover wherein the core is produced by vulcanizing a base rubber composition containing a butadiene rubber having a cis-polybutadiene structure content of not less than 90 percent before vulcanization. The amount of trans-polybutadiene structure present after vulcanization is 10 to 30 percent, as amounts over 30 percent are alleged to detrimentally result in cores that are too soft with deteriorated resilience performance, and to cause a decrease in golf ball performance. The core includes a vulcanizing agent, a filler, an organic peroxide, and an organosulfur compound.

British Patent No. 2,321,021 discloses a solid golf ball having a core and a cover formed on the core and having a two-layered cover construction having an inner cover layer and an outer cover layer. The outer cover layer is comprised of a rubber composite that contains 0.05 to 5 parts by weight of an organic sulfide compound. The core rubber composition comprises a base rubber, preferably 1,4-polybutadiene having a cis- content of at least 40 percent by weight, a crosslinking agent, a co-crosslinking agent, an organic sulfide, and a filler. The crosslinking agent is typically an organic peroxide present in an amount from 0.3 to 5.0 parts by weight and the co-crosslinking agent is typically a metal salt of an unsaturated fatty acid present in an

amount from 10 to 40 parts by weight. The organic sulfide compound is typically present from 0.05 to 5 parts by weight.

U.S. Patent No. 5,816,944 discloses a solid golf ball having a core and a cover wherein the core has a JIS-C hardness of 50 to 80 and the cover has a Shore-D hardness of 50 to 60. The core material includes vulcanized rubber, such as cis-polybutadiene, with a crosslinker, an organic peroxide, an organosulfur compound and/or a metal-containing organosulfur compound, and a filler.

Additionally, conventional polymers that have a high percentage of the trans-polybutadiene conformation, such as DIENE 35NF, from Firestone Corp., that has 40 percent cis- isomer and 50 percent trans-polybutadiene isomer, and mixtures of high-cis- and high-trans-polybutadiene isomers, such as CARIFLEX BR1220, from Shell Corporation, and FUREN 88, from Asahi Chemical Co., respectively, typically do not yield high resilience values and therefore are not desirable.

In addition to changing center or core ingredients to affect golf ball performance characteristics, a number of patents have issued that are directed towards modifying the properties of layers and covers used in forming a variety of golf balls, such as wound balls, conventional solid balls, multi-layer balls having dual cover layers, dual core layers, and/or balls having a mantle layer disposed between the cover and the core. The most common polymers used by manufacturers in golf ball layers and covers have been ionomers, such as SURLYN, commercially available from E.I. DuPont de Nemours and Co., of Wilmington, DE. Recently, however, manufacturers have investigated the used of alternative polymers, such as polyurethane. For example, U.S. Patent No. 3,147,324 is directed to a method of making a golf ball having a polyurethane cover.

Polyurethanes have been recognized as useful materials for golf ball covers since about 1960. Polyurethane is the product of a reaction between a polyurethane prepolymer and a curing agent. The polyurethane prepolymer is a product formed by a reaction between a polyol and a diisocyanate. The curing agents used previously are typically diamines or glycols. A catalyst is often employed to promote the reaction between the curing agent and the polyurethane prepolymer.

Since 1960, various companies have investigated the usefulness of polyurethane as a golf ball cover material. U.S. Patent No. 4,123,061 teaches a golf ball made from a polyurethane

prepolymer of polyether and a curing agent, such as a trifunctional polyol, a tetrafunctional polyol, or a diamine. U.S. Patent No. 5,334,673 discloses the use of two categories of polyurethane available on the market, i.e., thermoset and thermoplastic polyurethanes, for forming golf ball covers and, in particular, thermoset polyurethane covered golf balls made from a composition of polyurethane prepolymer and a slow-reacting amine curing agent, and/or a difunctional glycol. The first commercially successful polyurethane covered golf ball was the Titleist® Professional ball, first released in 1993.

Unlike SURLYN® or ionomer-covered golf balls, polyurethane golf ball covers can be formulated to possess the soft “feel” of balata covered golf balls. However, golf ball covers made from polyurethane have not, to date, fully matched SURLYN®-covered golf balls with respect to resilience or the rebound that is a function of the initial velocity of a golf ball after impact with a golf club.

U.S. Patent No. 3,989,568 discloses a three-component system employing either one or two polyurethane prepolymers and one or two polyols or fast-reacting diamine curing agents. The reactants chosen for the system must have different rates of reactions within two or more competing reactions.

U.S. Patent No. 4,123,061 discloses a golf ball made from a polyurethane prepolymer of polyether and a curing agent, such as a trifunctional polyol, a tetrafunctional polyol, or a fast-reacting diamine curing agent.

U.S. Patent No. 5,334,673 discloses a golf ball cover made from a composition of a polyurethane prepolymer and a slow-reacting polyamine curing agent and/or a difunctional glycol. Resultant golf balls are found to have improved shear resistance and cut resistance compared to covers made from balata or SURLYN®.

U.S. Patent No. 5,692,974 discloses methods of using cationic ionomers in golf ball cover compositions. Additionally, the patent relates to golf balls having covers and cores incorporating urethane ionomers. Improved resiliency and initial velocity are achieved by the addition of an alkylating agent such as t-butyl-chloride which induces ionic interactions in the polyurethane to produce cationic type ionomers.

International Patent Application WO 98/37929 discloses a composition for golf ball covers that comprises a blend of a diisocyanate/polyol prepolymer and a curing agent comprising a blend of

a slow-reacting diamine and a fast-reacting diamine. Improved "feel," playability, and durability characteristics are exhibited.

Conventional polyurethane elastomers are known to have lower resiliency than SURLYN® and other ionomer resins. It has now been discovered that the use of a polyurethane composition, according to the present invention, in forming golf ball cores, intermediate and mantle layers, and/or covers, can raise the velocity of a golf ball prepared with the composition: (1) closer to the velocities observed with SURLYN®-covered golf balls; and (2) higher than the velocities exhibited using alternative urethane compositions. Additionally, it is desired to combine polyurethane cover compositions with polybutadiene core materials, especially those having resilience indices greater than about 40. Cores formed of materials such as these have been found to provide exceptional resiliency characteristics without a loss in performance characteristics (*i.e.*, decreased compression).

A multi-layered core construction facilitates the ability to modify a ball's moment of inertia through the manipulation of the specific gravity of each individual core layer. By using a multi-layered core construction, a ball designer is able to control a ball's spin performance when hit with full shots. With full shots, the ball's inner construction greatly affects the ball's spin rate. Thus, the spin rate of driver and long iron shots can be controlled more precisely through use of multi-layer core technology. Further, the ball's feel can be influenced with greater control than can be achieved from a single solid core construction by modifying the hardness or compressibility of the individual layers.

Therefore, it is thus desired to prepare multi-layered golf balls having lower compression, while having the same or higher resilience than conventional balls. It is alternatively desired to obtain the same or lower compression while achieving greater resilience, both without undesirable decrease in velocity.

SUMMARY OF THE INVENTION

The present invention is directed to a golf ball comprising a core and a cover disposed about the core, wherein the core comprises a center and at least one outer core layer adjacent the center, and the cover comprises at least one inner cover layer and an outer cover layer; wherein the center has an outer diameter from about 0.375 in to about 1.4 in and deflection of greater than about 4.5 mm under a load of 100 Kg; the outer core layer has an outer diameter of from about

1.4 in to about 1.62 in; the inner cover layer has an outer diameter of greater than about 1.58 in and a material hardness of less than about 72 Shore D; and the outer cover layer has a hardness of greater than about 50 Shore D.

In one embodiment, the outer cover layer has a material hardness less than about 55 shore D and, preferably, the outer cover layer has a material hardness less than about 50 shore D. The inner cover layer should have a material hardness between about 60 and about 70 Shore D and, more preferably, between about 60 and about 65 Shore D.

In another embodiment, the inner cover layer outer diameter is from about 1.59 in to about 1.66 in and, more preferably, from about 1.6 in to about 1.64 in. The center outer diameter should be from about 0.5 in to about 1.25 in and, more preferably, from about 0.9 in to about 1.2 in. The outer core layer outer diameter should be from about 1.52 in to about 1.59 in and, more preferably, from about 1.535 in to about 1.58 in.

In yet another embodiment, the ball has a moment of inertia of less than about $83 \text{ g} \cdot \text{cm}^2$. Additionally, the center preferably has a first hardness, the outer core layer has a second hardness greater than the first, and the inner cover layer has a third hardness greater than the second. In a preferred embodiment, the outer cover layer has a fourth hardness less than the third hardness.

In one embodiment, the center has a first specific gravity and the outer core layer has a second specific gravity that differ by less than about 0.1. In a preferred embodiment, the center is solid. The center may also be liquid, hollow, or air-filled.

The present invention is also directed to a golf ball comprising a core and a cover disposed about the core, wherein the core comprises a solid center and an outer core layer adjacent the center, and the cover comprises an inner cover layer and an outer cover layer; wherein the center has an outer diameter from about 0.375 in to about 1.4 in and deflection of greater than about 4.5 mm under a load of 100 Kg; the outer core layer has an outer diameter of from about 1.4 in to about 1.62 in; the inner cover layer has an outer diameter of greater than about 1.58 in and a material hardness of less than about 72 Shore D; and the outer cover layer has a hardness of greater than about 50 Shore D.

In one embodiment, the outer cover layer has a material hardness of less than about 50 and a thickness of less than about 0.035 in. In a preferred embodiment, the center has a first hardness, the outer core layer has a second hardness greater than the first, and the inner cover

layer has a third hardness greater than the second. Additionally, the outer cover layer has a fourth hardness less than the third hardness.

In another embodiment, the inner cover layer outer diameter is from about 1.59 in to about 1.66 in and, preferably, from about 1.6 in to about 1.64 in. The center outer diameter should be from about 0.5 in to about 1.25 in and, preferably, from about 0.9 in to about 1.2 in. In yet another embodiment, the outer core layer outer diameter is from about 1.52 in to about 1.59 in. Additionally, the ball can have a moment of inertia of less than about $83 \text{ g}\cdot\text{cm}^2$. In another embodiment, the center has a first specific gravity and the outer core layer has a second specific gravity that differ by less than about 0.1.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a cross-sectional view of a golf ball having a dual cover and a dual core according to the invention.

DEFINITIONS

The term "about," as used herein in connection with one or more numbers or numerical ranges, should be understood to refer to all such numbers, including all numbers in a range.

As used herein, "cis-to-trans catalyst" means any component or a combination thereof that will convert at least a portion of cis-polybutadiene isomer to trans-polybutadiene isomer at a given temperature. It should be understood that the combination of the cis- isomer, the trans- isomer, and any vinyl- isomer, measured at any given time, comprises 100 percent of the polybutadiene.

As used herein, the term "active ingredients" is defined as the specific components of a mixture or blend that are essential to the chemical reaction.

As used herein, substituted and unsubstituted "aryl" groups means a hydrocarbon ring bearing a system of conjugated double bonds, typically comprising $4n + 2\pi$ ring electrons, where n is an integer. Examples of aryl groups include, but are not limited to phenyl, naphthyl, anisyl, tolyl, xylenyl and the like. According to the present invention, aryl also includes heteroaryl groups, e.g., pyrimidine or thiophene. These aryl groups may also be substituted with any number of a variety of functional groups. In addition to the functional groups described herein in connection with carbocyclic groups, functional groups on the aryl groups can include hydroxy

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and metal salts thereof; mercapto and metal salts thereof; halogen; amino, nitro, cyano, and amido; carboxyl including esters, acids, and metal salts thereof; silyl; acrylates and metal salts thereof; sulfonyl or sulfonamide; and phosphates and phosphites; and a combination thereof.

As used herein, the term "Atti compression" is defined as the deflection of an object or material relative to the deflection of a calibrated spring, as measured with an Atti Compression Gauge, that is commercially available from Atti Engineering Corp. of Union City, NJ. Atti compression is typically used to measure the compression of a golf ball. When the Atti Gauge is used to measure cores having a diameter of less than 1.680 in, it should be understood that a metallic or other suitable shim is used to make the diameter of the measured object 1.680 in. As used herein, substituted and unsubstituted "carbocyclic" means cyclic carbon-containing compounds, including, but not limited to cyclopentyl, cyclohexyl, cycloheptyl, adamantyl, and the like. Such cyclic groups may also contain various substituents in which one or more hydrogen atoms has been replaced by a functional group. Such functional groups include those described above, and lower alkyl groups having from 1-28 carbon atoms. The cyclic groups of the invention may further comprise a heteroatom.

As used herein, the term "coefficient of restitution" for golf balls is defined as the ratio of the rebound velocity to the inbound velocity when balls are fired into a rigid plate. The inbound velocity is understood to be 125 ft/s.

As used herein, the terms "Group VIA component" or "Group VIA element" mean a component that includes a sulfur component, a selenium component, or a tellurium component, or a combination thereof.

As used herein, the term "sulfur component" means a component that is elemental sulfur, polymeric sulfur, or a combination thereof. It should be further understood that "elemental sulfur" refers to the ring structure of S₈ and that "polymeric sulfur" is a structure including at least one additional sulfur relative to the elemental sulfur.

As used herein, the term "fluid" includes a liquid, a paste, a gel, a gas, or any combination thereof.

As used herein, the term "molecular weight" is defined as the absolute weight average molecular weight. The molecular weight is determined by the following method: approximately 20 mg of polymer is dissolved in 10 mL of tetrahydrofuran ("THF"), which may take a few days at room temperature depending on the polymer's molecular weight and distribution. One liter of

THF is filtered and degassed before being placed in a high-performance liquid chromatography (“HPLC”) reservoir. The flow rate of the HPLC is set to 1 mL/min through a Viscogel column. This non-shedding, mixed bed, column model GMHHR-H, which has an ID of 7.8 mm and 300 mm long is available from Viscotek Corp. of Houston, TX. The THF flow rate is set to 1 mL/min for at least one hour before sample analysis is begun or until stable detector baselines are achieved. During this purging of the column and detector, the internal temperature of the Viscotek TDA Model 300 triple detector should be set to 40°C. This detector is also available from Viscotek Corp. The three detectors (i.e., Refractive Index, Differential Pressure, and Light Scattering) and the column should be brought to thermal equilibrium, and the detectors should be purged and zeroed, to prepare the system for calibration according to the instructions provided with this equipment. A 100-μL aliquot of sample solution can then be injected into the equipment and the molecular weight of each sample can be calculated with the Viscotek’s triple detector software. When the molecular weight of the polybutadiene material is measured, a dn/dc of 0.130 should always be used. It should be understood that this equipment and these methods provide the molecular weight numbers described and claimed herein, and that other equipment or methods will not necessarily provide equivalent values as used herein.

As used herein, the term “multilayer” means at least two layers and includes liquid center balls, wound balls, hollow-center balls, and balls with at least two intermediate layers and/or an inner or outer cover.

As used herein, the term “thermoset” material refers to an irreversible, solid polymer that is the product of the reaction of two or more prepolymer precursor materials.

As used herein, the term “parts per hundred,” also known as “phr,” is defined as the number of parts by weight of a particular component present in a mixture, relative to 100 parts by weight of the total polymer component. Mathematically, this can be expressed as the weight of an ingredient divided by the total weight of the polymer, multiplied by a factor of 100.

As used herein, the term “substantially free” means less than about 5 weight percent, preferably less than about 3 weight percent, more preferably less than about 1 weight percent, and most preferably less than about 0.01 weight percent.

As used herein the term “resilience index” is defined as the difference in loss tangent measured at 10 cpm and 1000 cpm divided by 990 (the frequency span) multiplied by 100,000 (for normalization and unit convenience). The loss tangent is measured using an RPA 2000

manufactured by Alpha Technologies of Akron, OH. The RPA 2000 is set to sweep from 2.5 to 1000 cpm at a temperature of 100°C using an arc of 0.5 degrees. An average of six loss tangent measurements were acquired at each frequency and the average is used in calculation of the resilience index. The computation of resilience index is as follows:

$$\text{Resilience Index} = 100,000 \cdot [(\text{loss tangent @ 10 cpm}) - (\text{loss tangent @ 1000 cpm})]/990$$

DETAILED DESCRIPTION OF THE INVENTION

Referring to FIG. 1, a golf ball 10 of the present invention includes a core 12 and a cover 14 surrounding the core 12. The core 12 preferably comprises a center 16 and an outer core layer 18, and the cover 14 comprises an outer cover layer 20 and an inner cover layer 22.

The golf ball cores of the present invention may comprise any of a variety of constructions. For example, the core of the golf ball may comprise a conventional center surrounded by an intermediate mantle or outer core layer disposed between the center and the inner cover layer. The core may be a single layer or may comprise a plurality of layers. The innermost portion of the core may be solid or it may be a liquid filled sphere. As with the core, the intermediate mantle or outer core layer may also comprise a plurality of layers. The core may also comprise a solid or liquid filled center around which many yards of a tensioned elastomeric material are wound.

The materials for solid cores include compositions having a base rubber, a crosslinking agent, a filler, and a co-crosslinking or initiator agent. The base rubber typically includes natural or synthetic rubbers. A preferred base rubber is 1,4-polybutadiene having a cis-structure of at least 40%. Most preferably, the base rubber comprises high-Mooney-viscosity rubber. If desired, the polybutadiene can also be mixed with other elastomers known in the art such as natural rubber, polyisoprene rubber and/or styrene-butadiene rubber in order to modify the properties of the core.

The crosslinking agent includes a metal salt of an unsaturated fatty acid such as a zinc salt or a magnesium salt of an unsaturated fatty acid having 3 to 8 carbon atoms such as acrylic or methacrylic acid. Suitable cross linking agents include metal salt diacrylates, dimethacrylates and monomethacrylates wherein the metal is magnesium, calcium, zinc, aluminum, sodium, lithium or nickel.

One embodiment of the present invention relates to a multi-layer golf ball having a core comprising a solid center surrounded by at least one additional solid outer core layer. At least one of the outer core layers is formed of a resilient rubber-based component comprising a high-Mooney-viscosity rubber, and a crosslinking agent present in an amount from about 20 to about 40 parts per hundred, from about 30 to about 38 parts per hundred, and most preferably about 37 parts per hundred. It should be understood that the term "parts per hundred" is with reference to the rubber by weight.

The center of the ball is preferably solid having a resilient high-Mooney-viscosity rubber component, and a crosslinking agent present in an amount from about 15 to about 30 parts per hundred of the rubber, preferably in an amount from about 19 to about 25 parts per hundred of the rubber and most preferably having about 20 to 24 parts crosslinking agent per hundred of rubber.

The initiator agent can be any known polymerization initiator which decomposes during the cure cycle. Suitable initiators include peroxide compounds such as dicumyl peroxide, 1,1-di(t-butylperoxy) 3,3,5-trimethyl cyclohexane, a-a bis (t-butylperoxy) diisopropylbenzene, 2,5-dimethyl-2,5 di(t-butylperoxy) hexane or di-t-butyl peroxide and mixtures thereof.

As used herein, the term "filler" includes any compound or composition that can be used to vary the density and other properties of the core. Fillers typically include materials such as tungsten, zinc oxide, barium sulfate, silica, calcium carbonate, zinc carbonate regrind (recycled core material ground to 30 mesh particle), high-Mooney-viscosity rubber regrind, and the like.

The present invention also relates to multilayer golf balls having a core and a cover, such as a solid, hollow, or fluid-filled center, an outer core layer, and an inner and outer cover layer, disposed about the center. At least one of the center or intermediate layers includes a reaction product that includes a cis-to-trans catalyst, a resilient polymer component having polybutadiene, a free radical source, and optionally, a crosslinking agent, a filler, or both.

The invention also includes a method to convert the cis- isomer of the polybutadiene resilient polymer component to the trans- isomer during a molding cycle and to form a golf ball. Various combinations of polymers, cis-to-trans catalysts, fillers, crosslinkers, and a source of free radicals, may be used. To obtain a higher resilience and lower compression center or intermediate layer, a high-molecular weight polybutadiene with a cis- isomer content preferably greater than about 90 percent is converted to increase the percentage of trans- isomer content at

any point in the golf ball or portion thereof, preferably to increase the percentage throughout substantially all of the golf ball or portion thereof, during the molding cycle. More preferably, the cis-polybutadiene isomer is present in an amount of greater than about 95 percent of the total polybutadiene content. Without wishing to be bound by any particular theory, it is believed that a low amount of 1,2-polybutadiene isomer ("vinyl-polybutadiene") is desired in the initial polybutadiene, and the reaction product. Typically, the vinyl polybutadiene isomer content is less than about 7 percent. Preferably, the vinyl polybutadiene isomer content is less than about 4 percent. More preferably, the vinyl polybutadiene isomer content is less than about 2 percent. Without wishing to be bound by any particular theory, it is also believed that the resulting mobility of the combined cis- and trans-polybutadiene backbone is responsible for the lower modulus and higher resilience of the reaction product and golf balls including the same.

To produce a polymer reaction product that exhibits the higher resilience and lower modulus (low compression) properties that are desirable and beneficial to golf ball playing characteristics, high-molecular-weight cis-1,4-polybutadiene, preferably may be converted to the trans- isomer during the molding cycle. The polybutadiene material typically has a molecular weight of greater than about 200,000. Preferably, the polybutadiene molecular weight is greater than about 250,000, more preferably between about 300,000 and 500,000. Without wishing to be bound by any particular theory, it is believed that the cis-to-trans catalyst component, in conjunction with the free radical source, acts to convert a percentage of the polybutadiene polymer component from the cis- to the trans- conformation. The cis-to-trans conversion requires the presence of a cis-to-trans catalyst, such as an organosulfur or metal-containing organosulfur compound, a substituted or unsubstituted aromatic organic compound that does not contain sulfur or metal, an inorganic sulfide compound, an aromatic organometallic compound, or mixtures thereof. The cis-to-trans catalyst component may include one or more of the other cis-to-trans catalysts described herein.

In one embodiment, the at least one organosulfur component is substantially free of metal, which typically means less than about 10 weight percent metal, preferably less than about 3 weight percent metal, more preferably less than about 1 weight percent metal, and most preferably only trace amounts of metal, such as less than about 0.01 weight percent.

As used herein when referring to the invention, the term "organosulfur compound(s)" or "organosulfur component(s)," means at least one of 4,4'-diphenyl disulfide; 4,4'-ditolyl disulfide;

2,2'-benzamido diphenyl disulfide; bis(2-aminophenyl) disulfide; bis(4-aminophenyl) disulfide; bis(3-aminophenyl) disulfide; 2,2'-bis(4-aminonaphthyl) disulfide; 2,2'-bis(3-aminonaphthyl) disulfide; 2,2'-bis(4-aminonaphthyl) disulfide; 2,2'-bis(5-aminonaphthyl) disulfide; 2,2'-bis(6-aminonaphthyl) disulfide; 2,2'-bis(7-aminonaphthyl) disulfide; 2,2'-bis(8-aminonaphthyl) disulfide; 1,1'-bis(2-aminonaphthyl) disulfide; 1,1'-bis(3-aminonaphthyl) disulfide; 1,1'-bis(3-aminonaphthyl) disulfide; 1,1'-bis(4-aminonaphthyl) disulfide; 1,1'-bis(5-aminonaphthyl) disulfide; 1,1'-bis(6-aminonaphthyl) disulfide; 1,1'-bis(7-aminonaphthyl) disulfide; 1,1'-bis(8-aminonaphthyl) disulfide; 1,2'-diamino-1,2'-dithiodinaphthalene; 2,3'-diamino-1,2'-dithiodinaphthalene; bis(4-chlorophenyl) disulfide; bis(2-chlorophenyl) disulfide; bis(3-chlorophenyl) disulfide; bis(4-bromophenyl) disulfide; bis(2-bromophenyl) disulfide; bis(3-bromophenyl) disulfide; bis(4-fluorophenyl) disulfide; bis(4-iodophenyl) disulfide; bis(2,5-dichlorophenyl) disulfide; bis(3,5-dichlorophenyl) disulfide; bis(2,4-dichlorophenyl) disulfide; bis(2,6-dichlorophenyl) disulfide; bis(2,5-dibromophenyl) disulfide; bis(3,5-dibromophenyl) disulfide; bis(2-chloro-5-bromophenyl) disulfide; bis(2,4,6-trichlorophenyl) disulfide; bis(2,3,4,5,6-pentachlorophenyl) disulfide; bis(4-cyanophenyl) disulfide; bis(2-cyanophenyl) disulfide; bis(4-nitrophenyl) disulfide; bis(2-nitrophenyl) disulfide; 2,2'-dithiobenzoic acid ethylester; 2,2'-dithiobenzoic acid methylester; 2,2'-dithiobenzoic acid; 4,4'-dithiobenzoic acid ethylester; bis(4-acetylphenyl) disulfide; bis(2-acetylphenyl) disulfide; bis(4-formylphenyl) disulfide; bis(4-carbamoylphenyl) disulfide; 1,1'-dinaphthyl disulfide; 2,2'-dinaphthyl disulfide; 1,2'-dinaphthyl disulfide; 2,2'-bis(1-chlorodinaphthyl) disulfide; 2,2'-bis(1-bromonaphthyl) disulfide; 1,1'-bis(2-chloronaphthyl) disulfide; 2,2'-bis(1-cyanonaphthyl) disulfide; 2,2'-bis(1-acetylnaphthyl) disulfide; and the like; or a mixture thereof. Preferred organosulfur components include 4,4'-diphenyl disulfide, 4,4'-ditolyl disulfide, or 2,2'-benzamido diphenyl disulfide, or a mixture thereof. A more preferred organosulfur component includes 4,4'-ditolyl disulfide. The organosulfur cis-to-trans catalyst, when present, is preferably present in an amount sufficient to produce the reaction product so as to contain at least about 12 percent trans-polybutadiene isomer, but typically is greater than about 32 percent trans-polybutadiene isomer based on the total resilient polymer component. Suitable metal-containing organosulfur components include, but are not limited to, cadmium, copper, lead, and tellurium analogs of diethyldithiocarbamate, diamyldithiocarbamate, and dimethyldithiocarbamate, or mixtures thereof. Suitable substituted or unsubstituted aromatic organic components that do not include sulfur or a metal include, but

are not limited to, 4,4'-diphenyl acetylene, azobenzene, or a mixture thereof. The aromatic organic group preferably ranges in size from C₆ to C₂₀, and more preferably from C₆ to C₁₀. Suitable inorganic sulfide components include, but are not limited to titanium sulfide, manganese sulfide, and sulfide analogs of iron, calcium, cobalt, molybdenum, tungsten, copper, selenium, yttrium, zinc, tin, and bismuth. The cis-to-trans catalyst may also be a blend of an organosulfur component and an inorganic sulfide component.

The cis-to-trans catalyst can also include a Group VIA component, as defined herein. Elemental sulfur and polymeric sulfur are commercially available from, e.g., Elastochem, Inc. of Chardon, OH. Exemplary sulfur catalyst compounds include PB(RM-S)-80 elemental sulfur and PB(CRST)-65 polymeric sulfur, each of which is available from Elastochem, Inc. An exemplary tellurium catalyst under the tradename TELLOY and an exemplary selenium catalyst under the tradename VANDEX are each commercially available from RT Vanderbilt.

The cis-to-trans catalyst is preferably present in an amount from about 0.1 to 10 parts per hundred of the total resilient polymer component. More preferably, the cis-to-trans catalyst is present in an amount from about 0.1 to 5 parts per hundred of the total resilient polymer component. Most preferably, the cis-to-trans catalyst is present in an amount from about 0.1 to 8 parts per hundred of the total resilient polymer component. The cis-to-trans catalyst is typically present in an amount sufficient to produce the reaction product so as to increase the trans-polybutadiene isomer content to contain from about 5 percent to 70 percent trans-polybutadiene based on the total resilient polymer component.

The measurement of trans- isomer content of polybutadiene referred to herein was and can be accomplished as follows. Calibration standards are prepared using at least two polybutadiene rubber samples of known trans- content, e.g., high and low percent trans-polybutadiene). These samples are used alone and blended together in such a way as to create a ladder of trans-polybutadiene content of at least about 1.5 % to 50% or to bracket the unknown amount, such that the resulting calibration curve contains at least about 13 equally spaced points.

Using a commercially available Fourier Transform Infrared ("FTIR") spectrometer equipped with a Photoacoustic ("PAS") cell, a PAS spectrum of each standard was obtained using the following instrument parameters: scan at speed of 2.5 KHz (0.16 cm/s optical velocity), use a 1.2 KHz electronic filter, set an undersampling ratio of 2 (number of laser signal zero

crossings before collecting a sample), co-add a minimum of 128 scans at a resolution of 4 cm⁻¹ over a range of 375 to 4000 cm⁻¹ with a sensitivity setting of 1.

The cis-, trans-, and vinyl-polybutadiene peaks are typically found between 600 and 1100 cm⁻¹ in the PAS spectrum. The area under each of the trans-polybutadiene peaks can be integrated. Determining the fraction of each peak area relative to the total area of the three isomer peaks allow construction of a calibration curve of the trans-polybutadiene area fraction versus the actual trans-polybutadiene content. The correlation coefficient (R^2) of the resulting calibration curve must be a minimum of 0.95. A PAS spectrum is obtained, using the parameters described above, for the unknown core material at the point of interest (*e.g.*, the surface or center of the core) by filling the PAS cell with a sample containing a freshly cut, uncontaminated surface free of foreign matters, such as mold release and the like. The trans-polybutadiene area fraction of the unknown is analyzed to determine the actual trans-isomer content from the calibration curve.

In one known circumstance when barium sulfate is included, the above method for testing trans- content may be less accurate. Thus, an additional or alternative test of the trans- content of polybutadiene is as follows. Calibration standards are prepared using at least two polybutadienes of known trans- content (*e.g.*, high and low percent trans-polybutadiene). These samples are used alone and blended together in such a way as to create a ladder of trans-polybutadiene content of at least about 1.5 % to 50% or to bracket the unknown amount, such that the resulting calibration curve contains at least about 13 equally spaced points.

Using a Fourier Transform Raman ("FT-Raman") spectrometer equipped with a near-infrared laser, a Stokes Raman spectrum should be obtained from each standard using the following instrument parameters: sufficient laser power to obtain a good signal-to-noise ratio ("S/N") without causing excessive heating or fluorescence (typically about 400 to 800 mW is suitable); a resolution of 2 cm⁻¹; over a Raman shift spectral range of about 400 to 4000 cm⁻¹; and co-adding at least 300 scans.

A calibration curve may be constructed from the data generated above, using a chemometrics approach and software such as PLSplus/IQ from Galactic Industries Corp. of Salem, NH. An acceptable calibration was obtained with this software using a PLS-1 curve generated using an SNV (detrend) pathlength correction, a mean center data preparation, and a 5-

point SG second derivative over the spectral range from about 1600 to 1700 cm^{-1} . The correlation coefficient (R^2) of the resulting calibration curve must be a minimum of 0.95.

A Raman spectrum of the core material is obtained using this instrument at the point of interest in the sample (e.g., surface or center of the golf ball core). The sample must be free of foreign matter, such as mold release, etc. Analyze the spectrum of the sample using the PLS calibration curve to determine trans-polybutadiene isomer content of the sample.

A free-radical source, often alternatively referred to as a free-radical initiator, is required in the composition and method. The free-radical source is typically a peroxide, and preferably an organic peroxide. Suitable free-radical sources include di-t-amyl peroxide, di(2-t-butylperoxyisopropyl)benzene peroxide, 1,1-bis(t-butylperoxy)-3,3,5-trimethylcyclohexane, dicumyl peroxide, di-t-butyl peroxide, 2,5-di-(t-butylperoxy)-2,5-dimethyl hexane, n-butyl-4,4-bis(t-butylperoxy)valerate, lauryl peroxide, benzoyl peroxide, t-butyl hydroperoxide, and the like, and any mixture thereof. The peroxide is typically present in an amount greater than about 0.1 parts per hundred of the total resilient polymer component, preferably about 0.1 to 15 parts per hundred of the resilient polymer component, and more preferably about 0.2 to 5 parts per hundred of the total resilient polymer component. It should be understood by those of ordinary skill in the art that the presence of certain cis-to-trans catalysts according to the invention may require a larger amount of free-radical source, such as the amounts described herein, compared to conventional cross-linking reactions. The free radical source may alternatively or additionally be one or more of an electron beam, UV or gamma radiation, x-rays, or any other high energy radiation source capable of generating free radicals. It should be further understood that heat often facilitates initiation of the generation of free radicals.

Crosslinkers are included to increase the hardness of the reaction product. Suitable crosslinking agents include one or more metallic salts of unsaturated fatty acids or monocarboxylic acids, such as zinc, calcium, or magnesium acrylate salts, and the like, and mixtures thereof. Preferred acrylates include zinc acrylate, zinc diacrylate, zinc methacrylate, and zinc dimethacrylate, and mixtures thereof. The crosslinking agent must be present in an amount sufficient to crosslink a portion of the chains of polymers in the resilient polymer component. For example, the desired compression may be obtained by adjusting the amount of crosslinking. This may be achieved, for example, by altering the type and amount of crosslinking agent, a method well-known to those of ordinary skill in the art. The crosslinking

agent is typically present in an amount greater than about 0.1 percent of the resilient polymer component, preferably from about 10 to 40 percent of the resilient polymer component, more preferably from about 10 to 30 percent of the resilient polymer component. When an organosulfur is selected as the cis-to-trans catalyst, zinc diacrylate may be selected as the crosslinking agent and is present in an amount of less than about 25 phr.

Fillers added to one or more portions of the golf ball typically include processing aids or compounds to affect rheological and mixing properties, the specific gravity (*i.e.*, density-modifying fillers), the modulus, the tear strength, reinforcement, and the like. The fillers are generally inorganic, and suitable fillers include numerous metals or metal oxides, such as zinc oxide and tin oxide, as well as barium sulfate, zinc sulfate, calcium carbonate, barium carbonate, clay, tungsten, tungsten carbide, an array of silicas, and mixtures thereof. Fillers may also include various foaming agents or blowing agents which may be readily selected by one of ordinary skill in the art. Polymeric, ceramic, metal, and glass microspheres may be solid or hollow, and filled or unfilled. Fillers are typically also added to one or more portions of the golf ball to modify the density thereof to conform to uniform golf ball standards. Fillers may also be used to modify the weight of the center or at least one additional layer for specialty balls, *e.g.*, a lower weight ball is preferred for a player having a low swing speed.

The polymers, free-radical initiator, filler(s), and any other materials used in forming either the golf ball center or any portion of the core, in accordance with invention, may be combined to form a mixture by any type of mixing known to one of ordinary skill in the art. Suitable types of mixing include single pass and multi-pass mixing, and the like. The crosslinking agent, and any other optional additives used to modify the characteristics of the golf ball center or additional layer(s), may similarly be combined by any type of mixing. A single-pass mixing process where ingredients are added sequentially is preferred, as this type of mixing tends to increase efficiency and reduce costs for the process. The preferred mixing cycle is single step wherein the polymer, cis-trans catalyst, filler, zinc diacrylate, and peroxide are added sequentially. Suitable mixing equipment is well known to those of ordinary skill in the art, and such equipment may include a Banbury mixer, a two-roll mill, or a twin screw extruder. Conventional mixing speeds for combining polymers are typically used, although the speed must be high enough to impart substantially uniform dispersion of the constituents. On the other hand, the speed should not be too high, as high mixing speeds tend to break down the polymers being

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mixed and particularly may undesirably decrease the molecular weight of the resilient polymer component. The speed should thus be low enough to avoid high shear, which may result in loss of desirably high molecular weight portions of the polymer component. Also, too high a mixing speed may undesirably result in creation of enough heat to initiate the crosslinking before the preforms are shaped and assembled around a core. The mixing temperature depends upon the type of polymer components, and more importantly, on the type of free-radical initiator. For example, when using di(2-t-butyl-peroxyisopropyl)benzene as the free-radical initiator, a mixing temperature of about 80°C to 125°C, preferably about 88°C to 110°C, and more preferably about 90°C to 100°C, is suitable to safely mix the ingredients. Additionally, it is important to maintain a mixing temperature below the peroxide decomposition temperature. For example, if dicumyl peroxide is selected as the peroxide, the temperature should not exceed 200°F. Suitable mixing speeds and temperatures are well-known to those of ordinary skill in the art, or may be readily determined without undue experimentation.

The mixture can be subjected to, *e.g.*, a compression or injection molding process, to obtain solid spheres for the center or hemispherical shells for forming an intermediate layer. The polymer mixture is subjected to a molding cycle in which heat and pressure are applied while the mixture is confined within a mold. The cavity shape depends on the portion of the golf ball being formed. The compression and heat liberates free radicals by decomposing one or more peroxides, which may initiate the cis-to-trans conversion and crosslinking simultaneously. The temperature and duration of the molding cycle are selected based upon the type of peroxide and cis-trans catalyst selected. The molding cycle may have a single step of molding the mixture at a single temperature for a fixed time duration. An example of a single step molding cycle, for a mixture that contains dicumyl peroxide, would hold the polymer mixture at 340°F for a duration of 15 minutes. The molding cycle may also include a two-step process, in which the polymer mixture is held in the mold at an initial temperature for an initial duration of time, followed by holding at a second, typically higher temperature for a second duration of time. An example of a two-step molding cycle would be holding the mold at 290°F for 40 minutes, then ramping the mold to 340°F where it is held for a duration of 20 minutes. In a preferred embodiment of the current invention, a single-step cure cycle is employed. Single-step processes are effective and efficient, reducing the time and cost of a two-step process. The resilient polymer component, polybutadiene, cis-to-trans conversion catalyst, additional polymers, free-radical initiator, filler,

and any other materials used in forming either the golf ball center or any portion of the core, in accordance with the invention, may be combined to form a golf ball by an injection molding process, which is also well-known to one of ordinary skill in the art. Although the curing time depends on the various materials selected, a particularly suitable curing time is about 5 to 18 minutes, preferably from about 8 to 15 minutes, and more preferably from about 10 to 12 minutes. Those of ordinary skill in the art will be readily able to adjust the curing time upward or downward based on the particular materials used and the discussion herein.

The cured resilient polymer component, which contains a greater amount of trans-polybutadiene than the uncured resilient polymer component, is formed into an article having a first hardness at a point in the interior and a surface having a second hardness such that the second hardness differs from the first hardness by greater than 10 percent of the first hardness. Preferably, the article is a sphere and the point is the midpoint of the article. In another embodiment, the second hardness differs from the first by greater than 20 percent of the first hardness. The cured article also has a first amount of trans-polybutadiene at an interior location and a second amount of trans-polybutadiene at a surface location, wherein the first amount is at least about 6 percent less than the second amount, preferably at least about 10 percent less than the second amount, and more preferably at least about 20 percent less than the second amount. The interior location is preferably a midpoint and the article is preferably a sphere. The compression of the core, or portion of the core, of golf balls prepared according to the invention is preferably below about 50, more preferably below about 25.

The cover provides the interface between the ball and a club. Properties that are desirable for the cover are good moldability, high abrasion resistance, high tear strength, high resilience, and good mold release, among others. The cover typically has a thickness to provide sufficient strength, good performance characteristics and durability. The cover preferably has a thickness of less than about 0.1 in, more preferably, less than about 0.05 in, and most preferably, between about 0.02 and about 0.04 in. The invention is particularly directed towards a multilayer golf ball which comprises a core, an inner cover layer, and an outer cover layer. In this embodiment, preferably, at least one of the inner and outer cover layers has a thickness of less than about 0.05 in, more preferably between about 0.02 in and about 0.04 in. Most preferably, the thickness of either layer is about 0.03 in.

When the golf ball of the present invention includes an intermediate layer, such as an inner cover layer, this layer can include any materials known to those of ordinary skill in the art, including thermoplastic and thermosetting materials, but preferably the intermediate layer can include any suitable materials, such as ionic copolymers of ethylene and an unsaturated monocarboxylic acid which are available under the trademark SURLYN of E.I. DuPont de Nemours & Co., of Wilmington, DE, or IOTEK or ESCOR of Exxon. These are copolymers or terpolymers of ethylene and methacrylic acid or acrylic acid partially neutralized with salts of zinc, sodium, lithium, magnesium, potassium, calcium, manganese, nickel or the like, in which the salts are the reaction product of an olefin having from 2 to 8 carbon atoms and an unsaturated monocarboxylic acid having 3 to 8 carbon atoms. The carboxylic acid groups of the copolymer may be totally or partially neutralized and might include methacrylic, crotonic, maleic, fumaric or itaconic acid.

This golf ball can likewise include one or more homopolymeric or copolymeric inner cover layer materials, such as:

- (1) Vinyl resins, such as those formed by the polymerization of vinyl chloride, or by the copolymerization of vinyl chloride with vinyl acetate, acrylic esters or vinylidene chloride;
- (2) Polyolefins, such as polyethylene, polypropylene, polybutylene and copolymers such as ethylene methylacrylate, ethylene ethylacrylate, ethylene vinyl acetate, ethylene methacrylic or ethylene acrylic acid or propylene acrylic acid and copolymers and homopolymers produced using a single-site catalyst or a metallocene catalyst;
- (3) Polyurethanes, such as those prepared from polyols and diisocyanates or polyisocyanates and those disclosed in U. S. Patent No. 5,334,673;
- (4) Polyureas, such as those disclosed in U.S. Patent No. 5,484,870;
- (5) Polyamides, such as poly(hexamethylene adipamide) and others prepared from diamines and dibasic acids, as well as those from amino acids such as poly(caprolactam), and blends of polyamides with SURLYN, polyethylene, ethylene copolymers, ethyl-propylene-non-conjugated diene terpolymer, and the like;
- (6) Acrylic resins and blends of these resins with poly vinyl chloride, elastomers, and the like;
- (7) Thermoplastics, such as urethanes; olefinic thermoplastic rubbers, such as blends of polyolefins with ethylene-propylene-non-conjugated diene terpolymer; block copolymers of

styrene and butadiene, isoprene or ethylene-butylene rubber; or copoly(ether-amide), such as PEBAX, sold by ELF Atochem of Philadelphia, PA;

(8) Polyphenylene oxide resins or blends of polyphenylene oxide with high impact polystyrene as sold under the trademark NORYL by General Electric Company of Pittsfield, MA;

(9) Thermoplastic polyesters, such as polyethylene terephthalate, polybutylene terephthalate, polyethylene terephthalate/glycol modified and elastomers sold under the trademarks HYTREL by E.I. DuPont de Nemours & Co. of Wilmington, DE, and LOMOD by General Electric Company of Pittsfield, MA;

(10) Blends and alloys, including polycarbonate with acrylonitrile butadiene styrene, polybutylene terephthalate, polyethylene terephthalate, styrene maleic anhydride, polyethylene, elastomers, and the like, and polyvinyl chloride with acrylonitrile butadiene styrene or ethylene vinyl acetate or other elastomers; and

(11) Blends of thermoplastic rubbers with polyethylene, propylene, polyacetal, nylon, polyesters, cellulose esters, and the like.

Preferably, the optional intermediate layer includes polymers, such as ethylene, propylene, butene-1 or hexane-1 based homopolymers or copolymers including functional monomers, such as acrylic and methacrylic acid and fully or partially neutralized ionomer resins and their blends, methyl acrylate, methyl methacrylate homopolymers and copolymers, imidized, amino group containing polymers, polycarbonate, reinforced polyamides, polyphenylene oxide, high impact polystyrene, polyether ketone, polysulfone, poly(phenylene sulfide), acrylonitrile-butadiene, acrylic-styrene-acrylonitrile, poly(ethylene terephthalate), poly(butylene terephthalate), poly(ethylene vinyl alcohol), poly(tetrafluoroethylene) and their copolymers including functional comonomers, and blends thereof. Suitable cover compositions also include a polyether or polyester thermoplastic urethane, a thermoset polyurethane, a low modulus ionomer, such as acid-containing ethylene copolymer ionomers, including E/X/Y terpolymers where E is ethylene, X is an acrylate or methacrylate-based softening comonomer present in about 0 to 50 weight percent and Y is acrylic or methacrylic acid present in about 5 to 35 weight percent. More preferably, in a low spin rate embodiment designed for maximum distance, the acrylic or methacrylic acid is present in about 16 to 35 weight percent, making the ionomer a

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high modulus ionomer. In a higher spin embodiment, the inner cover layer includes an ionomer where an acid is present in about 10 to 15 weight percent and includes a softening comonomer.

The cover preferably include a polyurethane composition comprising the reaction product of at least one polyisocyanate, polyol, and at least one curing agent.

Any polyisocyanate available to one of ordinary skill in the art is suitable for use according to the invention. Exemplary polyisocyanates include, but are not limited to, 4,4'-diphenylmethane diisocyanate ("MDI"), polymeric MDI, carbodiimide-modified liquid MDI, 4,4'-dicyclohexylmethane diisocyanate ("H12MDI"), p-phenylene diisocyanate ("PPDI"), toluene diisocyanate ("TDI"), 3,3'-dimethyl-4,4'-biphenylene diisocyanate ("TODI"), isophoronediiisocyanate ("IPDI"), hexamethylene diisocyanate ("HDI"), naphthalene diisocyanate ("NDI"); xylene diisocyanate ("XDI"); para-tetramethylxylene diisocyanate ("p-TMXDI"); meta-tetramethylxylene diisocyanate ("m-TMXDI"); ethylene diisocyanate; propylene-1,2- diisocyanate; tetramethylene-1,4-diisocyanate; cyclohexyl diisocyanate; 1,6-hexamethylene- diisocyanate ("HDI"); dodecane-1,12-diisocyanate; cyclobutane-1,3-diisocyanate; cyclohexane-1,3- diisocyanate; cyclohexane-1,4- diisocyanate; 1-isocyanato-3,3,5-trimethyl-5- isocyanatomethylcyclohexane; methyl cyclohexylene diisocyanate; triisocyanate of HDI; triisocyanate of 2,4,4-trimethyl- 1,6-hexane diisocyanate ("TMDI"), tetracene diisocyanate, naphthalene diisocyanate, anthracene diisocyanate, and mixtures thereof. Polyisocyanates are known to those of ordinary skill in the art as having more than one isocyanate group, e.g., di-, tri-, and tetra-isocyanate. Preferably, the polyisocyanate includes MDI, PPDI, TDI, or a mixture thereof, and more preferably, the polyisocyanate includes MDI. It should be understood that, as used herein, the term "MDI" includes 4,4'-diphenylmethane diisocyanate, polymeric MDI, carbodiimide-modified liquid MDI, and mixtures thereof and, additionally, that the diisocyanate employed may be "low free monomer," understood by one of ordinary skill in the art to have lower levels of "free" monomer isocyanate groups, typically less than about 0.1% free monomer groups. Examples of "low free monomer" diisocyanates include, but are not limited to Low Free Monomer MDI, Low Free Monomer TDI, and Low Free Monomer PPDI.

The at least one polyisocyanate should have less than about 14% unreacted NCO groups. Preferably, the at least one polyisocyanate has no greater than about 7.5% NCO, and more preferably, less than about 7.0%.

Any polyol available to one of ordinary skill in the art is suitable for use according to the invention. Exemplary polyols include, but are not limited to, polyether polyols, hydroxy-terminated polybutadiene (including partially/fully hydrogenated derivatives), polyester polyols, polycaprolactone polyols, and polycarbonate polyols. In one preferred embodiment, the polyol includes polyether polyol. Examples include, but are not limited to, polytetramethylene ether glycol ("PTMEG"), polyethylene propylene glycol, polyoxypropylene glycol, and mixtures thereof. The hydrocarbon chain can have saturated or unsaturated bonds and substituted or unsubstituted aromatic and cyclic groups. Preferably, the polyol of the present invention includes PTMEG.

In another embodiment, polyester polyols are included in the polyurethane material of the invention. Suitable polyester polyols include, but are not limited to, polyethylene adipate glycol, polybutylene adipate glycol, polyethylene propylene adipate glycol, ortho-phthalate-1,6-hexanediol, and mixtures thereof. The hydrocarbon chain can have saturated or unsaturated bonds, or substituted or unsubstituted aromatic and cyclic groups.

In another embodiment, polycaprolactone polyols are included in the materials of the invention. Suitable polycaprolactone polyols include, but are not limited to, 1,6-hexanediol-initiated polycaprolactone, diethylene glycol initiated polycaprolactone, trimethylol propane initiated polycaprolactone, neopentyl glycol initiated polycaprolactone, 1,4-butanediol-initiated polycaprolactone, and mixtures thereof. The hydrocarbon chain can have saturated or unsaturated bonds, or substituted or unsubstituted aromatic and cyclic groups.

In yet another embodiment, the polycarbonate polyols are included in the polyurethane material of the invention. Suitable polycarbonates include, but are not limited to, polyphthalate carbonate. The hydrocarbon chain can have saturated or unsaturated bonds, or substituted or unsubstituted aromatic and cyclic groups. In one embodiment, the molecular weight of the polyol is from about 200 to about 4000.

Polyamine curatives are also suitable for use in the polyurethane composition of the invention and have been found to improve cut, shear, and impact resistance of the resultant balls. Preferred polyamine curatives include, but are not limited to, 3,5-dimethylthio-2,4-toluenediamine and isomers thereof; 3,5-diethyltoluene-2,4-diamine and isomers thereof, such as 3,5-diethyltoluene-2,6-diamine; 4,4'-bis-(sec-butylamino)-diphenylmethane; 1,4-bis-(sec-butylamino)-benzene, 4,4'-methylene-bis-(2-chloroaniline); 4,4'-methylene-bis-(3-chloro-2,6-

diethylaniline); polytetramethyleneoxide-di-p-aminobenzoate; N,N'-dialkyldiamino diphenyl methane; p,p'-methylene dianiline ("MDA"); m-phenylenediamine ("MPDA"); 4,4'-methylene-bis-(2-chloroaniline) ("MOCA"); 4,4'-methylene-bis-(2,6-diethylaniline); 4,4'-diamino-3,3'-diethyl-5,5'-dimethyl diphenylmethane; 2,2', 3,3'-tetrachloro diamino diphenylmethane; 4,4'-methylene-bis-(3-chloro-2,6-diethylaniline); trimethylene glycol di-p-aminobenzoate; and mixtures thereof. Preferably, the curing agent of the present invention includes 3,5-dimethylthio-2,4-toluenediamine and isomers thereof, such as ETHACURE 300, commercially available from Albermarle Corporation of Baton Rouge, LA. Suitable polyamine curatives, which include both primary and secondary amines, preferably have molecular weights ranging from about 64 to about 2000.

At least one of a diol, triol, tetraol, or hydroxy-terminated curatives may be added to the aforementioned polyurethane composition. Suitable diol, triol, and tetraol groups include ethylene glycol; diethylene glycol; polyethylene glycol; propylene glycol; polypropylene glycol; lower molecular weight polytetramethylene ether glycol; 1,3-bis(2-hydroxyethoxy) benzene; 1,3-bis-[2-(2-hydroxyethoxy) ethoxy] benzene; 1,3-bis-{2-[2-(2-hydroxyethoxy) ethoxy] ethoxy} benzene; 1,4-butanediol; 1,5-pentanediol; 1,6-hexanediol; resorcinol-di-(β -hydroxyethyl) ether; hydroquinone-di-(β -hydroxyethyl) ether; and mixtures thereof. Preferred hydroxy-terminated curatives include ethylene glycol; diethylene glycol; 1,4-butanediol; 1,5-pentanediol; 1,6-hexanediol, trimethylol propane, and mixtures thereof.

Preferably, the hydroxy-terminated curatives have molecular weights ranging from about 48 to 2000. It should be understood that molecular weight, as used herein, is the absolute weight average molecular weight and would be understood as such by one of ordinary skill in the art.

Both the hydroxy-terminated and amine curatives can include one or more saturated, unsaturated, aromatic, and cyclic groups. Additionally, the hydroxy-terminated and amine curatives can include one or more halogen groups. The polyurethane composition can be formed with a blend or mixture of curing agents. If desired, however, the polyurethane composition may be formed with a single curing agent.

Any method known to one of ordinary skill in the art may be used to combine the polyisocyanate, polyol, and curing agent of the present invention. One commonly employed method, known in the art as a one-shot method, involves concurrent mixing of the polyisocyanate, polyol, and curing agent. This method results in a mixture that is inhomogenous

(more random) and affords the manufacturer less control over the molecular structure of the resultant composition. A preferred method of mixing is known as a prepolymer method. In this method, the polyisocyanate and the polyol are mixed separately prior to addition of the curing agent. This method affords a more homogeneous mixture resulting in a more consistent polymer composition.

An optional filler component may be chosen to impart additional density to blends of the previously described components. The selection of such filler(s) is dependent upon the type of golf ball desired (i.e., one-piece, two-piece multi-component, or wound). Examples of useful fillers include zinc oxide, barium sulfate, calcium oxide, calcium carbonate and silica, as well as the other well known corresponding salts and oxides thereof. Additives, such as nanoparticles, glass spheres, and various metals, such as titanium and tungsten, can be added to the polyurethane compositions of the present invention, in amounts as needed, for their well-known purposes. Additional components which can be added to the polyurethane composition include UV stabilizers and other dyes, as well as optical brighteners and fluorescent pigments and dyes. Such additional ingredients may be added in any amounts that will achieve their desired purpose. Due to the very thin nature, it has been found by the present invention that the use of a castable, reactive material, which is applied in a fluid form, makes it possible to obtain very thin outer cover layers on golf balls. Specifically, it has been found that castable, reactive liquids, which react to form a urethane elastomer material, provide desirable very thin outer cover layers.

The castable, reactive liquid employed to form the urethane elastomer material can be applied over the inner core using a variety of application techniques such as spraying, dipping, spin coating, or flow coating methods which are well known in the art. An example of a suitable coating technique is that which is disclosed in U.S. Patent Number 5,733,428, filed May 2, 1995 entitled "Method And Apparatus For Forming Polyurethane Cover On A Golf Ball", the disclosure of which is hereby incorporated by reference in its entirety in the present application.

The cover is preferably formed around the inner cover layer by mixing and introducing the material in the mold halves. It is important that the viscosity be measured over time, so that the subsequent steps of filling each mold half, introducing the core into one half and closing the mold can be properly timed for accomplishing centering of the core cover halves fusion and achieving overall uniformity. Suitable viscosity range of the curing urethane mix for introducing

cores into the mold halves is determined to be approximately between about 2,000 cP and about 30,000 cP, with the preferred range of about 8,000 cP to about 15,000 cP.

To start the cover formation, mixing of the prepolymer and curative is accomplished in motorized mixer including mixing head by feeding through lines metered amounts of curative and prepolymer. Top preheated mold halves are filled and placed in fixture units using pins moving into holes in each mold. After the reacting materials have resided in top mold halves for about 40 to about 80 seconds, a core is lowered at a controlled speed into the gelling reacting mixture. At a later time, a bottom mold half or a series of bottom mold halves have similar mixture amounts introduced into the cavity.

A ball cup holds the ball core through reduced pressure (or partial vacuum) in hose. Upon location of the coated core in the halves of the mold after gelling for about 40 to about 80 seconds, the vacuum is released allowing core to be released. The mold halves, with core and solidified cover half thereon, are removed from the centering fixture unit, inverted and mated with other mold halves which, at an appropriate time earlier, have had a selected quantity of reacting polyurethane prepolymer and curing agent introduced therein to commence gelling.

Similarly, U.S. Patent No. 5,006,297 to Brown *et al.* and U.S. Patent No. 5,334,673 to Wu both also disclose suitable molding techniques which may be utilized to apply the castable reactive liquids employed in the present invention. Further, U.S. Patent Nos. 6,180,040 and 6,180,722 disclose methods of preparing dual core golf balls. The disclosures of these patents are hereby incorporated by reference in their entirety. However, the method of the invention is not limited to the use of these techniques.

Depending on the desired properties, balls prepared according to the invention can exhibit substantially the same or higher resilience, or coefficient of restitution ("COR"), with a decrease in compression or modulus, compared to balls of conventional construction. Additionally, balls prepared according to the invention can also exhibit substantially higher resilience, or COR, without an increase in compression, compared to balls of conventional construction. Another measure of this resilience is the "loss tangent," or $\tan \delta$, which is obtained when measuring the dynamic stiffness of an object. Loss tangent and terminology relating to such dynamic properties is typically described according to ASTM D4092-90. Thus, a lower loss tangent indicates a higher resiliency, thereby indicating a higher rebound capacity. Low loss tangent indicates that most of the energy imparted to a golf ball from the club is converted to

dynamic energy, *i.e.*, launch velocity and resulting longer distance. The rigidity or compressive stiffness of a golf ball may be measured, for example, by the dynamic stiffness. A higher dynamic stiffness indicates a higher compressive stiffness. To produce golf balls having a desirable compressive stiffness, the dynamic stiffness of the crosslinked reaction product material should be less than about 50,000 N/m at -50°C. Preferably, the dynamic stiffness should be between about 10,000 and 40,000 N/m at -50°C, more preferably, the dynamic stiffness should be between about 20,000 and 30,000 N/m at -50°C.

The resultant golf balls typically have a coefficient of restitution of greater than about 0.7, preferably greater than about 0.75, and more preferably greater than about 0.78. The golf balls also typically have an Atti compression of at least about 40, preferably from about 50 to 120, and more preferably from about 60 to 100. The golf ball polybutadiene material of the present invention typically has a flexural modulus of from about 500 psi to 300,000 psi, preferably from about 2000 to 200,000 psi. The golf ball polybutadiene material typically has a hardness of at least about 15 Shore A, preferably between about 30 Shore A and 80 Shore D, more preferably between about 50 Shore A and 60 Shore D.

The specific gravity of the center composition is typically greater than about 0.7 and preferably greater than about 1.0. The center and the outer core layer may have the same or different specific gravity values. In one embodiment, the center and outer core layer have different specific gravity values. It is preferred, however, that the specific gravity of the outer core layer and the center differ by less than 0.1.

The center composition should comprise at least one rubber material having a resilience index of at least about 40. Preferably the resilience index is at least about 50. Polymers that produce resilient golf balls and, therefore, are suitable for the present invention, include but are not limited to CB23, CB22, BR60, and 1207G. To clarify the method of computation for resilience index, the resilience index for CB23, for example, is computed as follows:

$$\text{Resilience Index for CB23} = 100,000 \cdot [(0.954)-(0.407)]/990$$

$$\text{Resilience Index for CB23} = 55$$

The molding process and composition of golf ball portions typically results in a gradient of material properties. Methods employed in the prior art generally exploit hardness to quantify

these gradients. Hardness is a qualitative measure of static modulus and does not represent the modulus of the material at the deformation rates associated with golf ball use, *i.e.*, impact by a club. As is well known to one skilled in the art of polymer science, the time-temperature superposition principle may be used to emulate alternative deformation rates. For golf ball portions including polybutadiene, a 1-Hz oscillation at temperatures between 0°C and -50°C are believed to be qualitatively equivalent to golf ball impact rates. Therefore, measurement of loss tangent and dynamic stiffness at 0°C to -50°C may be used to accurately anticipate golf ball performance, preferably at temperatures between about -20°C and -50°C.

Additionally, the unvulcanized rubber, such as polybutadiene, in golf balls prepared according to the invention typically has a Mooney viscosity of between about 40 and about 80, more preferably, between about 45 and about 60, and most preferably, between about 45 and about 55. Mooney viscosity is typically measured according to ASTM D-1646.

When golf balls are prepared according to the invention, they typically will have dimple coverage greater than about 60 percent, preferably greater than about 65 percent, and more preferably greater than about 75 percent. The flexural modulus of the cover on the golf balls, as measured by ASTM method D6272-98, Procedure B, is typically greater than about 500 psi, and is preferably from about 500 psi to 150,000 psi. As discussed herein, the outer cover layer is preferably formed from a relatively soft polyurethane material. In particular, the material of the outer cover layer should have a material hardness, as measured by ASTM-2240, preferably less than about 60 Shore D, more preferably less than about 55 Shore D, and most preferably less than about 50 Shore D. The outer cover layer hardness, as measured on the golf ball, is preferably greater than about 50. The inner cover layer preferably has a material hardness less than 72 Shore D, more preferably less than about 70 Shore D, and most preferably, less than about 68 Shore D. It is preferred that the center, outer core layer, and inner cover layer each have a different hardness and more preferably, that the hardness progressively increases away from the center until reaching the outer cover layer, *i.e.*, the outer core layer is harder than the center and the inner cover layer is harder than the outer core layer.

The overall outer diameter ("OD") of the center is preferably from about 0.375 in to about 1.4 in, more preferably from about 0.5 in to about 1.25 in, and most preferably from about 0.9 in to about 1.2 in. The OD of the outer core layer is preferably from about 1.4 in to about 1.62 in, more preferably from about 1.52 in to about 1.59 in, and most preferably from about

1.535 in to about 1.58 in. The OD of the inner cover layer of the golf balls of the present invention is preferably greater than about 1.58 in, more preferably from about 1.59 in to about 1.66 in, and most preferably from about 1.6 in to about 1.64 in.

The present multilayer golf ball can have an overall diameter of any size. Although the United States Golf Association ("USGA") specifications limit the minimum size of a competition golf ball to 1.680 in. There is no specification as to the maximum diameter. Golf balls of any size, however, can be used for recreational play. The preferred diameter of the present golf balls is from about 1.680 in to about 1.800 in. The more preferred diameter is from about 1.680 in to about 1.760 in. The most preferred diameter is about 1.680 in to about 1.740 in.

The golf balls of the present invention should have a moment of inertia ("MOI") of less than about 83 and, preferably, less than about 82. The MOI is typically measured on model number MOI-005-104 Moment of Inertia Instrument manufactured by Inertia Dynamics of Collinsville, CT. The instrument is plugged into a PC for communication via a COMM port and is driven by MOI Instrument Software version #1.2.

The golf balls of the present invention should have a center deflection of greater than about 4.5 mm under a load of 100 Kg. Preferably, the center deflection is greater than about 4.8 mm and, more preferably, about 5.0 mm under a load of 100 Kg. The deflection data is measured with a Stable Micro Systems, Materials Master, (model number MT-LQ) instrument commercially available from Mono Research Labs. The MT-LQ is equipped with a 500 Kg load cell, which begins measuring deflection when 60 g is placed on it.

Prior to measuring deflection, the platens are calibrated. After calibration, the operator places the sphere to be measured on the surface of the bottom platen. The top platen moves down with a crosshead speed of one in/min. When the surface of the top platen contacts the sphere and reaches a compressive force of 60 g (the trigger force), the displacement is measured as a function of force, with force being the independent variable on the x axis. The instrument measures a predetermined number of data points/min which result in a plot of displacement versus force, from which the displacement of the sphere at a load of 100 Kg can be determined.

EXAMPLE

Two golf balls were prepared according to the present invention and are designated VDC45 and VDC48 in Table I below. The VDC golf balls contained a core formed of a 1.0-in-diameter solid center and an outer core layer having a thickness of 0.275 in to form a core having an outer diameter of 1.55 in. The core was surrounded by an inner cover layer having a thickness of 0.035 in and an outer cover layer having a thickness of 0.030 in, to provide a golf ball outer diameter of 1.68 in. A control golf ball was prepared according to conventional technology. The control ball was formed of a solid core having a diameter of 1.550 in, an inner cover layer having a thickness of 0.035 in, and an outer cover layer having a thickness of 0.030 in, to provide a golf ball outer diameter of 1.68 in. The center compositions for both golf balls are presented below in Table I.

TABLE I

Center Composition	VDC45	VDC48	Control
CB23	100.0	100.0	100.0
zinc diacrylate	25.05	25.05	27.0
zinc oxide	5.26	5.26	4.3
di-tolyl disulfide	0.63	0.63	-
DCP-70 ¹	2.0	2.0	-
tungsten	33.4	33.4	12.74
color dispersion	0.07	0.07	0.14
Trigonox-265 ²	-	-	0.53

¹ DCP-70 is dicumyl peroxide on a binder in pellet and is commercially available from Elastochem, Inc. of Chardon, OH

² a peroxide mixture on filler commercially available from Akzo Nobel Chemicals Inc. of Chicago, IL

The outer core layer composition for both VDC balls comprises high-Mooney-viscosity CB23 polybutadiene, zinc diacrylate, zinc oxide, DCP-70, Kurary TP 251, Varox 231XL, and a color dispersion. The inner cover layers were the same construction for both VDC balls and the control ball. The inner cover layers were formed of a 50/50 Na/Li blend of SURLYN® 8945 and SURLYN® 7940. The outer cover layer of the VDC45 ball comprises a PMS1088 prepolymer, commercially available from Polyurethane Specialties Co. (77.8%) cured with

*was this an
admission of
prior art*

Ethacure 300, commercially available from Albemarle Corp. (18.7%), and white dispersion, commercially available from Harwich Chemical (3.5%).

The outer cover layer of the VDC48 ball comprises a Vibrathane B-625 prepolymer, commercially available from Uniroyal (80.5%; NCO level: 6.1-6.6%) cured with Ethacure 300, commercially available from Albemarle Corp. (16%), and white dispersion, commercially available from Harwich Chemical (3.5%).

The VDC balls were formed in two different constructions, one with an outer cover layer having a material Shore D hardness of about 45, and a second with an outer cover layer having a material Shore D hardness of about 48. The VCD balls were tested for a variety of golf ball properties, such as ball compression, center hardness (interior and surface), core layer hardness, inner cover layer hardness, cover hardness, and compared to the Control ball, also tested for the same properties.

TABLE II

	VDC45	VDC48	Control
Ball Properties			
Ball Compression (Atti)	96	96	85
Center - surface hardness ¹ (Shore C)	73.3	73.3	
Outer Core Layer hardness ¹ (Shore C)	83.3	83.3	
Inner Cover Layer hardness ¹ (Shore D)	62.8	62.8	
Cover hardness ¹ (Shore D)	56	58	57
moment of inertia (g-cm ²)	80.73	80.73	81.11
CoR	0.815	0.817	0.815

¹ hardness measured directly on the golf ball (as compared to material hardness)

The launch angle and spin were measured for both VDC balls and the Control ball, for a variety of golf clubs. The data for each ball, off of each club type, are presented below in Table III.

TABLE III

Club: Pro Driver ¹	Launch Angle (°)	Spin (rpm)
VDC45	9.5	3072
VDC48	9.3	3134
Control	9.2	3357
Club: Standard Driver ²		
VDC45	9.1	3091
VDC48	9.1	3038
Control	9.0	3370
Club: 8-Iron ³		
VDC45	19.3	7035
VDC48	19.6	6863
Control	18.9	7457
Club: Wedge ⁴		
VDC45	25.5	9335
VDC48	25.5	9290
Control	25.0	9623

¹ Ball Speed: 167; Launch Angle: 9°; Spin Rate: 3500 rpm; Club: Driver; Club Head: 975D; Loft: 7.5°; Shaft: Graphite Design YS9-X

² Ball Speed: 160 mph; Launch Angle: 9.5°; Spin Rate: 3000 rpm; Club: Driver; Club Head: 975D; Loft: 8.5°; Shaft: X100

³ Ball Speed: 115 mph; Launch Angle: 18.5°; Spin Rate: 9000 rpm; Club: 8-iron; Club Head: DCI Black; Loft: 40°; Shaft: X100

⁴ Ball Speed: 95; Launch Angle: 24°; Spin Rate: 10400 rpm; Club: wedge; Club Head: DCI Black; Loft: 46°; Shaft: X-100

It is clear from the data presented in Table III, that the golf ball of the present invention decreases driver spin for both a Pro driver and a Standard driver. One of ordinary skill in the art is well aware that decreasing driver spin to optimize flight increases distance off the tee. Too much 8-iron spin can make approach shots into the green difficult to control whereas wedge spin

is important to making approach shots stop at desired locations on the green, especially when a player is pitching or chipping to the green.

The invention described and claimed herein is not to be limited in scope by the specific embodiments herein disclosed, since these embodiments are intended as illustrations of several aspects of the invention. Any equivalent embodiments are intended to be within the scope of this invention. Indeed, various modifications of the invention in addition to those shown and described herein will become apparent to those skilled in the art from the foregoing description. Such modifications are also intended to fall within the scope of the appended claims.

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